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Grindability determination of torrefied biomass materials using the Hybrid Work Index

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HIGHLIGHTS

- A work index was developed called the Hybrid Work Index for biomass materials.
- The HWI was shown to be sensitive to heat treatment and energy input.
- The comminution order was shown to be sensitive to degree of treatment.
- The HWI equation was shown to produce a relative grinding energy.
- Further study could lead to an industrial standard for treated biomass materials.

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ABSTRACT

The grindability of torrefied biomass materials is a difficult parameter to evaluate due to its inhomogeneous character and non-uniform morphology. However, it is necessary to develop a grinding test that is representative of the wide ranging character of biomass and torrefied biomass materials. Previous research has shown that Resistance to Impact Milling (RIM) can be linearly correlated to thermally driven weight loss in biomass. In particular, the RIM equipment was found to supply the right energy level to physically break down structurally deficient biomass materials while leaving the un-touched material relatively intact [1–3]. However, the RIM procedure was not designed to extract the comminution energy. Alternatively, the Bond Work Index (BWI) procedure was developed to accurately assess the grinding energy of brittle materials [4,5]. However, the milling energy is too low to be effective for biomass comminution. In this research, the BWI procedure was utilized with the ball–mill approach in the RIM test to evaluate torrefied biomass materials. The hybridized procedure has been shown to be both highly correlated to energy consumption and sensitive to degree of torrefaction. The proposed Hybrid Work Index (HWI) is certainly useful for assessing torrefaction in a laboratory environment, but it may also be correlated to grinding energy at industrial scales.

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1. Introduction

Torrefaction technology, as a promising way to improve fuel properties, was developed in the 1980s by Pechiney, a French company, to commercially convert wood into torrefied wood. They used torrefied wood to replace charcoal for the production of metals from metal oxides. This heat treatment process uses inert gas to drive out the moisture, gases, and volatile organic compounds (VOCs) [6–9].

Torrefied biomass retains most of its chemical energy and is resistant to moisture and decay. Moreover, it loses its visco-plastic properties, becomes brittle and can grind easily. When biomass is heated up to 160 °C, it loses water and retains its physical and mechanical properties. As the temperature rises to between 180 °C and 280 °C, moisture, carbon dioxide, large amounts of acetic acid and low weight VOCs are removed, producing a hydrophobic solid product with an increased energy density (on a mass basis) and greatly increased grindability [10–14]. In general, energy consumption for size reduction of torrefied wood is 50–85% smaller in comparison with fresh wood [15,16]. That said, a grinding index suitable for heat-treated biomass materials has not been developed and standardized. In particular, the widely varying hardness, brittleness, and visco-plastic properties of raw, partially treated, and fully treated biomass make a single test that can predict grinding energy in a large-scale system for every level of heat treatment and kind of biomass difficult to achieve. In an attempt to develop such a test, we have taken the approach of combining two established methods.

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The first method is the Resistance to Impact Milling (RIM). The RIM test was developed in Germany to determine the amount of fungal decay in wood [2]. The RIM is a test of the mechanical strength of raw and fungal decayed biomass. Fungal decayed wood is much weaker than raw wood and is more susceptible to fragmentation by impact. The RIM test is conducted by loading a high-energy, planetary ball mill with carefully prepared wood samples and monitoring the rate of decay by splitting the product into three size fractions. As a batch process, the mill contents of RIM test are always changing and the associated grinding energy is not constant. The test works because the energy level is high enough to quickly fragment any mechanically compromised material but low enough that the non-compromised material degrades very slowly. In the research to develop the RIM test, the researchers compared fungal decay to thermal decay and found that the RIM test produced the same result in many cases. It has been theorized that this behavior is due to the fact that both low temperature heat treatments (torrefaction) and certain fungal activity decay the raw biomass by degradation of hemicellulose. The success of the RIM test in correlating weight loss in both fungal and heat treated samples to mechanical degradation led us to select the high-energy, planetary ball mill as the test platform for a grindability test as various levels of treatment could be distinguished.

The other method combined was the Bond Work Index (BWI) [4,5]. The BWI was developed to assess the grinding energy of materials with brittle fracture characteristics. The BWI test has been standardized and uses a rotary ball mill with defined dimensions, media size, and volume fractions. The test works by counting the number of revolutions it takes to produce a certain fraction of undersized materials in a semi-batch recycle loop. A semi-batch recycle loop closely approximates a continuous grinding circuit. In essence, the BWI works because there is a definable and uniform energy put into the mill for every mill revolution and the semi-batch recycle loop ensures that the mill loading and particle size remain nearly constant as the system reaches steady-state.

The goal of this research is to take the equipment used in the RIM test and combine it with a slightly modified BWI procedure to create a grinding index that can be used for the wide range of biomass materials such that they could be used as coal substitutes. The hybridized method is referred to as the Hybrid Work Index (HWI).

2. Theory

All common work indices, including the BWI, are derived from the general comminution energy equation:

$$\frac{dE}{dx} = -cx^{-n} \tag{1}$$

Here, dE is the infinitesimal specific energy needed to fracture a particle distribution and shift the characteristic size, x, by an infinitesimal amount. Both c and n are constants. It is assumed that the entire distribution shifts by dx when dE is put into the system. Therefore, how characteristic values are chosen is not important as long as it is consistent. A positive energy value results in a decreasing particle size so energy input to the system is positive.

dE is integrated from the characteristic feed size (x_f) to the characteristic product size (x_p).

$$E = \int_{x_f}^{x_p} -cx^{-n}dx = \frac{-c}{1-n}\left(x_p^{1-n} - x_f^{1-n}\right) = \frac{c}{n-1}\left(\frac{1}{x_p^{n-1}} - \frac{1}{x_f^{n-1}}\right) \tag{2}$$

In order to maintain the right physical understanding, x_f and x_p are positive, non-zero values and $x_p < x_f$ which bounds n to be greater than one, exclusive. If n is one or less, the system will generate energy by fracture rather than consume it.

The concept of the work index is now introduced. The work index is the amount of specific energy needed to take a feed distribution with a characteristic size of infinity, and reduce it to a defined size, γ. By assigning the energy needed to accomplish this theoretical comminution to W_i and substituting infinity and γ into the feed and product sizes in Eq. (2), the work index is obtained.

$$W_i = \frac{c}{n-1}\left(\frac{1}{\gamma^{n-1}}\right) \tag{3}$$

Dividing Eq. (2) by Eq. (3) yields the generalized work index equation used in the most common work indices, such as the BWI.

$$E = W_i\gamma^{n-1}\left(\frac{1}{x_p^{n-1}} - \frac{1}{x_f^{n-1}}\right) \tag{4}$$

The familiar BWI equation is obtained when n is set to 1.5, the characteristic product size, γ, is set to 100 μm, and the distributions are measured at the 80% passing level (commonly demarcated by the subscript 80).

$$E = 10W_i\left(\frac{1}{\sqrt{x_{p80}}} - \frac{1}{\sqrt{x_{f80}}}\right) \tag{5}$$

Direct measurements of W_i are not possible as obtaining a feed with an infinite size is not possible. However, it is possible to evaluate the other three variables in Eq. (5) and calculate W_i.

The BWI test procedure has become a widely used standard test in industry and is useful because it approximates the energy needed in large-scale, continuous systems [17,18]. One important difference between the BWI the HWI procedure developed here is the kind of mill used. The BWI uses a horizontal axis, slowly rotating ball mill and the number of turns are counted to determine the energy input. Because of the high energy needed to fragment biomass, this was not practical. Instead, the HWI uses a high-energy, planetary ball mill. Though the mills differ, the fact that a given unit of energy is input to the system for every revolution remains true. That said, counting the revolutions is not practical with such high speed mills. Instead, the time is recorded and the rotation is kept constant, thus we can substitute the measured power of the mill, P, multiplied by time of operation, t, for the energy term in Eqs. (4) and (5). Further, we will make it more convenient by selecting $\gamma = 1$ and not assuming an n value. Thus the general work index can be defined as:

$$W_i = \frac{E}{\left(\frac{1}{x_p^{n-1}} - \frac{1}{x_f^{n-1}}\right)} = \frac{p \times t_e/m_s}{\left(\frac{1}{x_p^{n-1}} - \frac{1}{x_f^{n-1}}\right)} \tag{6}$$

Here, E is the mass specific grinding energy which is expanded as the power transferred to the sample, P, multiplied by the equilibrium time, t_e, divided by the sample mass, m_s.

The comminution order, n, can be determined by integrating Eq. (1) and dividing through by power, P.

$$t = \frac{\int_{x_f}^{x_p} -cx^{-n}dx}{P} = A - \frac{B}{1-n}x^{1-n} \tag{7}$$

Thus, to evaluate n, the characteristic size, x, must be measured as a function of time of grinding. A t vs x plot can be compiled and curve fit. To find the correct n, a value can be assumed and A and B can be co-varied in a solver to find the minimum residual. n can then be varied and the residuals compared. The correct value of n will be taken as the value that results in the minimum total residual.

The HWI can then be defined by dividing Eq. (6) through by the power term, P. This is valid as P is truly not measurable and is a function of the specific mill used, the rotation characteristics, dimensions, efficiencies, etc. It is possible to measure the net electrical power to the mill, but not the power being transferred to the sample. Thus, the HWI is mill specific (as any work index truly is) and a mill factor, α_m, must be used should a different mill be used to measure the true HWI and each mill must be calibrated to each other using a standard material or two batches of the same material. Thus the HWI is defined in Eq. (8).

$$HWI = \frac{\alpha_m W_i}{P_s} = \frac{\alpha_m \times t/m_s}{\left(\frac{1}{x_p^{n-1}} - \frac{1}{x_f^{n-1}}\right)} \tag{8}$$

Here, P_s represents the power transferred to the sample to achieve the size reduction in a standard mill type. α_m is thus dimensionless and represents the ratio of any given mill power input to the standard power, P_s. Once a standard mill is defined and agreed upon, the α_m factor for that mill will be set to unity. While this work is the first to publish the method for the HWI, the mill used may not be the mill used to define a standard. However, for the purposes of this work, it will be assumed that α_m, is unity. If a different mill is picked as a standard later, the α_m factor for this work will have to be adjusted. Further, the mill factor will allow the results of the lab-scale test to be applied to a large-scale mill and will serve as a relation factor to relate the HWI to other work indices, such as the BWI. Thus three factors should be reported with any materials measured with the HWI procedure, the HWI value, the α_m value, and the n value. It should also be noted that the HWI has the dimensions of time per unit mass and the units should also be reported. With this understanding, the HWI represents the time it takes to take a sample of infinite size to a size of 1 μm normalized by a mass if the grinding is done in a standard mill, which is yet to be defined.

3. HWI test procedure

3.1. Equipment

Several pieces of equipment were used for sample preparation and HWI tests. The entire batch of light and dark pine was ground using a disk grinder (BICO Inc. Pulverizer, Model: Type UA) with a pre-set gap of 3 mm. A tap density tester (GlobePharma, Model: ETD-1020) was used to determine density of the samples. An automated sieve machine (W.S. Tyler Rotap, Model: RX-29) was used to separate biomass materials to various size ranges. A riffle splitter (Humbolt, Model: H39-75) was used to split biomass samples into two equal portions and ensure uniform distribution of subsamples. A planetary ball mill (MTI Corp, Model: MSK-SFM-1) was used for the HWI procedure. The planetary ball mill has stations for four milling pots. Each pot is stainless steel with an inside diameter of 84 mm and a height of 100 mm. The mean rotation speed of the pots around the primary drive axis is 290RPM. The planetary rotation is 580RPM. The planetary gear ratio is fixed and the machine controls the rotation to within 10%.

3.2. Sample preparation

Two samples of torrefied Loblolly Pine (Pinus taeda) were selected for this initial study. They were obtained from the North Carolina State University, Forestry Extension and were the product of their torrefaction system [19]. The samples differ by the amount of time spent in the semi-industrial process. The first sample had a relatively short retention time and was characterized as a lightly torrefied material (hereafter referred to as ‘‘Light Pine’’). The second sample spent a longer time in the unit and was characterized as a heavily torrefied material (hereafter referred to as ‘‘Dark Pine’’). While no further characterization was available for these samples, it is sufficient to say that one was much more heavily reacted than the other, and it is instructive to demonstrate the utility of the HWI to differentiate between various levels of torrefaction. Access to well characterized torrefied samples is limited at this time. Future work will include correlation to weight loss, chemical composition, and large-scale grinding.

The BICO disk mill with the milling gap set to 3 mm was used to produce starting material. The mill product was size segregated at US 6 mesh (3.35 mm) using a Rotap. The undersized material was taken as the product and the oversize material was reground until it passed the sieve. The sample was well mixed and divided into smaller lots that were approximately 100 ml in size. At least five of the samples were checked in Tap Density Tester to determine the material density. If the measured densities differed by more than 2%, the samples were remixed and split again. If the densities were consistent, the sample was considered well mixed and work continued. Once the sample was well mixed, the density was used to calculate the mass needed to fill 30% volume of the mill pots and recorded as m_s. From the well mixed lot, a subsample equal to $16^* m_s$ was separated, again using the riffle. From this sub-sample, 16 smaller samples were produced by riffle splitting. The weight deviation of each fraction was not more than 1%.

3.3. Pre-grinding curve

A pre-grinding curve was constructed prior to the HWI testing. The pre-grinding curve is done in a batch fashion and used to estimate a starting grind time and help determine further grinding times to reach a steady-state. The following outlines the procedure used:

1. One of the 16 sub samples was charged to a mill pot.
2. A set of stainless steel balls were charged to the mill (2 × 19.5 mm, 2 × 10.0 mm, and 4 × 6.0 mm).
3. The mill was run for a short time and the time recorded as t_1.
4. The material was discharged from the mill and sieved at US Std 70 mesh (212 μm).
5. The undersized mass was recorded as m_1.
6. The sample was recharged to the mill and run for another time, t_{i+1} (i stands for iteration).
7. That undersized mass was recorded as m_{i+1}.
8. Steps 6 and 7 were repeated, increasing i with each step until ~40% passing was reached.
9. The data were plotted as t_i vs m_i and a curve was fit to the data.
10. Using this curve, the initial time to produce 25% passing was calculated and recorded t_s.

This information is not critical to the success of the test, but is useful for gauging the initial run time for the grindability testing and for picking the evaluation times to reach steady-state.

3.4. HWI grindability procedure

The HWI procedure is much like the BWI procedure in that one uses a semi-batch process to approximate a continuous operation. The approximation is accomplished by repeatedly grinding, sieving, recycling the oversize and adding make-up fresh feed until a steady-state is attained. In the case of the HWI, one is interested in finding the steady-state grind time rather than the number of mill revolutions as in the BWI.

The planetary ball mill contains four pots, which allows four parallel tests to be run at the same time. The procedures used to determine the HWI are as follows:

1. 3 of the 16 samples with mass, m_s, were used to determine the 50% passing feed size.
2. 8 of the 16 samples were split twice to generate 32, 1/4 ms samples and each was checked for consistency.

3. 4 of the 16 samples with masses within 1% of m_s were charged to the mill pots (1 in each).
4. The standard load of steel balls (same as used in pre-grinding) was charged to each pot.
5. The material was ground for time t_s as determined from the pre-grinding curve.
6. The material was discharged from each pot and sieved separately at 70 US mesh using the Rotap
7. The undersized material was collected and massed. The oversize was returned to the mill pot it came from.
8. Fresh feed from the samples prepared in step 2 was added to the mill pots equal to the mass of undersized removed from each pot. If the amount needed was less than 1/4 m_s, the sample was riffle split to obtain the right mass.
9. Steps 5 to 8. were repeated
10. A new grinding time (t_{i+1}) was calculated based on the percentage passing (X_n), the current iteration grind time (t_i), and the starting grind time (t_s) using Eqs. (8) and (9)
11. The material was reground with a grinding time of (t_{i+1}) and steps 6, 7, 8 and 10 were repeated until X_n was within 1% of 25%.
12. The mill undersized material was kept and analyzed for the 50% passing size.
13. Based on the feed and the product size measured and the steady-state grind time determined by linear regression, the HWI was calculated using Eq. (6).

Because of the iterative method, the mill contents continue to shift until a steady-state loading is achieved, which is necessarily different from a batch loading for the same grind time. The feed material is inhomogeneous. Some of the material degrades quite rapidly, while other material degrades quite slowly. Therefore, the mill contents will change during each iteration and will accumulate more of the material that is difficult to mill as compared to the feed material. Thus, the grinding time will necessarily increase to obtain the same percentage passing. After the first iteration, the percentage passing drops significantly, as expected. The time selected for the next iteration must be larger than the previous time. A somewhat empirical method was used to select the next time. At a given time, the pre-grinding curve can relate a percentage passing at a given iteration, X_n, to a time value, t_n, which is necessarily lower than the pre-grinding time to 25% passing, t_s. Because the pre-grinding curve was determined under batch conditions and the HWI is conducted at semi-batch conditions, the current iteration time, t_i, must be greater than t_n. It is assumed that the percentage passing at steady-state is a linear function of time (close approximation). Further, at steady-state, $t_n = t_s$, $t_i = t_{i+1}$, and $X_n = 25\%$, necessarily. This is depicted graphically in Fig. 1.

As can be seen, the group of points (t_n,ln(X_n)), (t_n,0), and (t_i,0) form a triangle as do (t_s,ln(25)), (t_s,0), and (t_{i+1},0) and that the angular relationships of the triangles allow for one to use similarity relationships to relate the sides. Thus the following relationship holds:

$$t_{i+1} = \frac{\ln(25)}{\ln(X_n)}(t_i - t_n) + t_s \tag{9}$$

$$t_n = \exp(\alpha \times \ln(X_n) + \beta) \tag{10}$$

Here the α and β values are the slope and intercept of the log–log plot of the pre-grinding curve respectively (Fig. 4). Starting with a $t_{i=1}$ value equal to t_s ensures that the steady-state is approached from the lower time value and that when the percentage passing value reaches 25% that the system is at steady-state (or very near to it) as the system approaches the steady-state time asymptotically. When the percentage passing reaches 25%, the associated time represents the time needed to take a sample of mass m_s and reduce it from a feed size of x_f to a product size of x_p. Because of the semi-batch process used to determine the time, the contents in the mill should be relatively constant as should the power input into the mill and the efficiency of the energy transfer to the material in the mill. Thus the experimentally determined time should be directly proportional to the specific grinding energy.

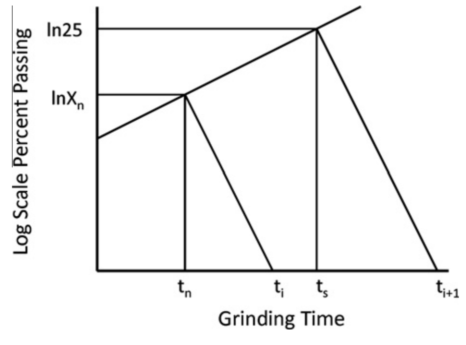

Fig. 1. Geometric representation of time selection algorithm.

4. Results

4.1. Sample preparation

It was very important that the sample was prepared carefully so that any sample/sub-sample was as uniform and representative of the whole as possible. More variation existing in the feed material bulk properties will result in greater experimental error in determination of the steady-state time. For this reason, the material was ground to pass a 3 mm sieve, carefully mixed, and split with a riffle.

After the material was ground to pass 3 mm, it was mixed and riffle split until the standard deviation of the bulk density of the measured sub-samples was within 2% using a tap density tester in accordance with ASTM D7481-09 [20]. The results are shown in Table 1. Bulk density was selected as a uniformity measurement because the material properties that affect the grindability are also reflected in the density. Reducing the variation farther is difficult as the starting sample size is relatively large (1–3 mm) and the sample volume is relatively small (~100 ml).

Following a uniform split, 3 of the samples were taken to have the particle size measured via the QICPIC™ at NETL. The QICPIC™ is an image based particle size analyzer manufactured by Sympatec GmbH [21]. The method used to analyze the particle size is somewhat arbitrary, but should be consistent throughout the tests. The QICPIC™ was chosen because it was available, was quick, and easy to use. Fig. 2 shows the measured pre-HWI test particle size

Table 1
Density (g/ml) of torrefied pine.

Sample	Dark pine	Light pine
1	0.319	0.274
2	0.327	0.276
3	0.324	0.269
4	0.316	0.266
5	0.315	0.267
6	0.314	0.273
7	0.328	0.269
8	0.324	0.272
Average	0.321	0.271
Standard deviation	1.74%	1.31%
30% Mill filling Wt	57.616 g	48.608 g
m_s	14.404 g	12.152 g

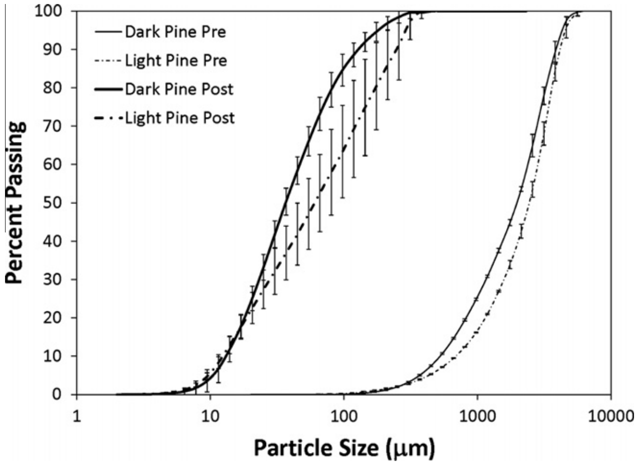

Fig. 2. Cumulative PSDs for dark and light pine pre-ground to 3 mm passing and post-ground after the HWI test.

distribution for the dark and light pine samples after being ground and sieved to pass a 3 mm screen and the post HWI test particle size of the sub 70 mesh material.

For the HWI testing, the representative size chosen was the 50% passing value. Table 2 shows the measured size for each sample as well as the 95% confidence interval. As can be seen, the pre-HWI material sizes were significantly different from each other after being pre-ground with the same disk spacing. The smaller size for the Dark Pine sample gives the first indication that the Dark Pine sample is easier to grind than the Light Pine sample. The post HWI test samples also show that the light pine was more difficult to grind in the fact that at the same cut size, the average particle size was noticeably larger (however, the statistical significance is much lower than the feed). There was greater variability in the light pine post sample than the dark pine. The post test measurements represent the average size and 95% confidence of the sub 70 mesh material collected from the four pots after the HWI test had reached steady-state. The values in Table 2 were used to calculate the HWI grindability index for each sample.

4.2. Pre-grinding curve

Each sample was run in a batch mode according to the above outlined procedure. For the purpose of demonstration, the pre-grinding test was repeated multiple times for each sample, which allows one to gauge the repeatability and uniformity of the samples. The dark pine sample was run twice with good repeatability. The light pine sample was run four times and the results show comparable repeatability. Fig. 3 shows the data collected. The data markers represent the average value at each time. The error bars represent the 95% confidence interval. The error in time of milling is minimal as each sample was run on a timer. As can be seen, each data set can be closely approximated with a power law curve, and there is a significant difference in the grindability of each sample.

Using the data in Fig. 3, a ln(time) vs ln(%passing) diagram was compiled, and a best fit line was constructed using the least squared error technique. The parameters used in Eq. (10) as well as the determined starting time are shown in Table 3.

Table 2
50% Passing feed size (μm) for HWI test.

	Average size	95% Confidence interval
Dark pine pre	1970.3	29.45
Light pine pre	2434.3	80.90
Dark pine post	36.7	2.67
Light pine post	60.7	20.8

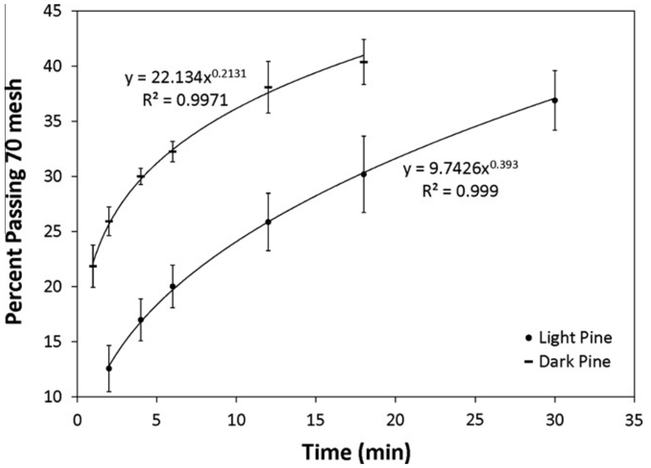

Fig. 3. Pre-grinding curves of 3.35 mm torrefied pine.

4.3. Determination of comminution order

According to Eq. (7), the time to grind a material should vary according to an inverse power of the characteristic size. Further, it would be expected that similar materials would have the same comminution order, *n*, but may vary in the impact efficiency constant (*c* in Eq. (1) and *B* in Eq. (7)). That is, the fragmentation occurs in the same manner, but may vary in the number/energy of impacts needed to achieve the same result. The integration constant, *A*, collects the variation in starting size. Thus the two treated pine materials were repeatedly ground and sized to check both for similar fragmentation behavior and to attain the appropriate grinding order. The representative size chosen was the mean particle size at 50% passing as determined by the QICPIC™. The cumulative grinding time was plotted against the 50% passing mean particle size. The integration constant, *A*, and the impact efficiency constant, *B*, were solved for using the minimization of squared error technique and the grinding order, *n*, was swept across reasonable values. Fig. 5 and Table 4 show the data and fitted values.

The grinding orders for each sample were determined by fitting parameters *A* and *B* to the collected data while sweeping across a set of *n* values. The residuals were monitored and plotted as a function of the comminution order. A polynomial fit was made for each data set, and the value for *n* was chosen so that the residuals would be minimized. The residual plots and data fits are shown in Fig. 6.

There is a definite and significant difference between the light pine and dark pine samples with the dark pine (more embrittled material) having a lower grinding order. That said, the grinding order suggests that the change in energy with comminution of these materials is not proportional to the diameter (as with Kick's law), proportional to crack length (as in Bond's law) or even proportional to the surface area (as with Rittinger's law), but in some way proportional to something between surface area and volume [22]. The fact that the comminution order lies between 2 and 3 suggests that the absorption of energy throughout the entire volume of a particle

Table 3
Pre-grinding parameters.

Sample	α	β	t_s
Light pine	2.5420	−5.7849	11.00
dark pine	4.6795	−14.489	1.77

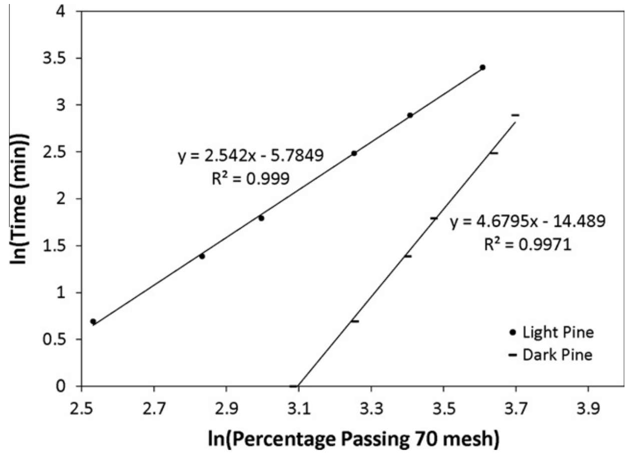

Fig. 4. Logarithm pre-grinding curves of 3.35 mm torrefied pine.

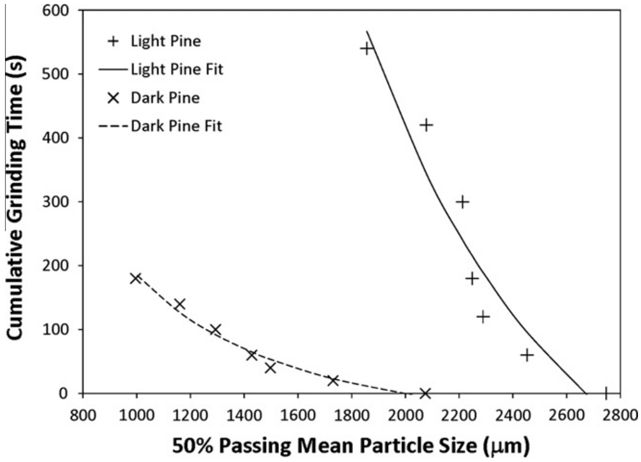

Fig. 5. Cumulative grinding time vs 50% passing mean particle size.

Table 4
Comminution order parameters.

Sample	*A*	*B*	*n*
Light Pine	−535.35	7.5945×10^9	3.00
Dark Pine	−97.27	2.0445×10^7	2.56

dominates the crushing energy absorbed by the particle. This leads one to believe that visco-plastic deformation is very important in the grinding of these materials and that, even when heat treated, they retain some degree of the original elasticity/plasticity. The fact that upon greater degrees of heat treatment, one finds that the grinding order decreases, suggest that the visco-plastic behavior is lessening in importance and that the formation of new surface area is important.

While the cause for such high order comminution is not yet understood, it is clear that the comminution order must be dependent on the degree of heat treatment. It should be possible to relate the comminution order to the mass loss of a given species of biomass during heat treatment. That said, developing the functional form that relates these two observations is beyond the scope of the current work and will be addressed in further research. For now, it will be taken that the light pine sample has a comminution order of 3.00 and the dark pine, 2.56.

4.4. Hybrid Work Index determination

With the samples carefully prepared and the information shown in Table 3, it was possible to execute the HWI Grindability Procedure, defined above. Tables 5 and 6 show the results of the testing as per the HWI Grindability Procedure. The tables list the iteration number, the time the sample was ground and the mass of sample that passed a US standard 70 mesh sieve after each iteration. The percentages represent the amount of sample passing the sieve relative to the total sample mass in the mill. The last two columns show the average amount passing in all four mill pots and the associated 95% confidence interval.

To calculate the steady-state grinding time, the grinding time was plotted against the average mass passing the 70 mesh sieve, as seen in Fig. 7. The information was found to be generally linear. However, there did seem to be some oscillation in the data about the line, especially for points far away from equilibrium. Proving the significance of this would be difficult as a best fit line generally fell within the 95% confidence interval of the percent passing 70 mesh data. If there is a trend, it seemed to be more pronounced and significant with the light pine sample.

The unfilled markers represent the grind time vs average percent passing data in Tables 5 and 6. The horizontal error bars represent the deviation 95% confidence interval expressed as a percentage. The filled markers are the accepted values for the grind time. The vertical error bars represent the 95% confidence interval of the error in the time values determined for the last three data points as compared to the best fit line. Only the last three data points were used because they were the closest values to equilibrium. The accepted steady-state grinding time and 95% confidence interval for each sample are shown in Table 7 (See Table 8).

As can be seen, there is a significant and large difference between the steady-state grinding time for the dark and light pine values. The light pine takes is nearly 5.7 times longer to grind to the same mesh size.

The last piece of information needed to evaluate Eq. (8) is the 50% passing size of the ground sample. Though the post test particle size is chronologically the last piece of information gathered, it is shown here in Fig. 2 and Table 2 for the sake of brevity. With the mill factor assumed to be unity, time in seconds and mass in kilograms, the HWI can be calculated and is shown in for the materials in this study. The difference in the HWI value is clearly significant. The effect of comminution order is also clearly shown as the numerical difference between the HWI values is a factor of nearly 88.

It is tempting to compare HWI values and associate that directly with grinding energy. However, one can only do that if the comminution order is the same. Without knowing that, the comparison will not be valid. Therefore, HWI values should never be reported for biomass materials without also reporting the comminution order.

5. Discussion

The character of industrially torrefied pine can be quite varied. Within the same sample one can find individual pieces with widely varying character. Fig. 8 shows individual pieces picked out of the light pine sample before testing and Fig. 9 shows optical micrographs of representative, epoxy mounted cross-sections. Clearly, the time/temperature profile that each particle experiences within the same mechanism is different as the character of individual particles in the same batch is so vastly different. However, even if the particles experienced the same time/temperature history, the results would still vary considerably from particle to particle because of the wide variety of sizes and shapes. The heat transfer to each particle has to occur from the outside in, thus each particle will

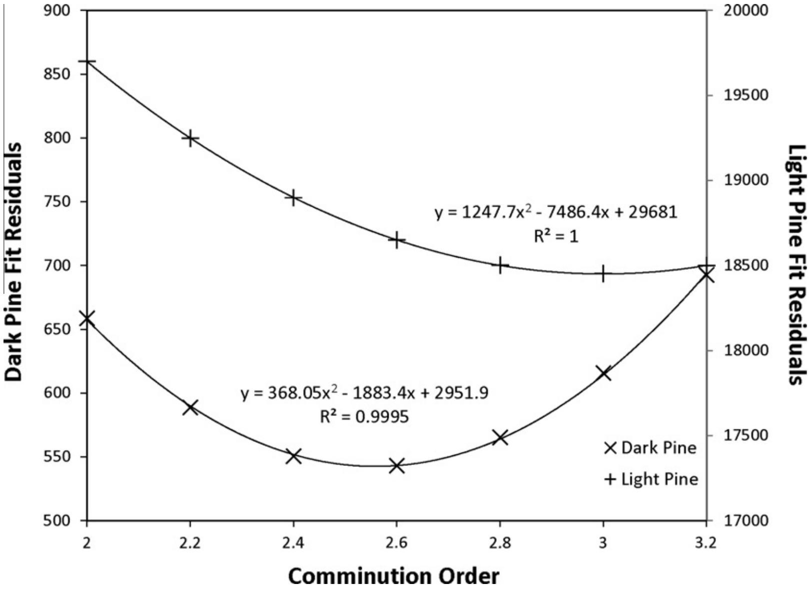

Fig. 6. Comminution order residuals.

Table 5
HWI Test results, dark pine.

Iteration	Grinding time (min)	Mass of undersize mill 1 (g)	Mass of undersize mill 2 (g)	Mass of undersize mill 3 (g)	Mass of undersize mill 4 (g)	Average (g)	95% Confidence (g)
0	1.77	14.711 (25.53%)	15.133 (26.27%)	13.800 (23.95%)	15.529 (26.48%)	14.726 (25.56%)	1.454
1	1.77	7.708 (13.38%)	8.024 (13.93%)	8.264 (14.43%)	8.456 (14.68%)	8.113 (14.08%)	0.632
2	3.09	8.475 (14.71%)	8.535 (14.81%)	8.366 (14.52%)	8.943 (15.52%)	8.580 (14.89%)	0.494
3	5.27	10.108 (17.54%)	10.345 (17.96%)	9.833 (17.15%)	10.935 (18.98%)	10.318 (17.91%)	0.919
4	7.25	11.569 (20.08%)	12.164 (21.11%)	11.311 (19.63%)	12.638 (21.93%)	11.921 (20.69%)	1.170
5	8.64	11.573 (20.09%)	12.556 (21.79%)	12.618 (21.90%)	12.816 (22.24%)	12.391 (21.51%)	1.090
6	9.92	12.705 (22.05%)	13.015 (22.59%)	12.305 (21.36%)	12.723 (22.08%)	12.687 (22.02%)	0.572
7	11.08	12.914 (22.41%)	12.632 (21.92%)	13.300 (23.08%)	12.705 (22.05%)	12.888 (22.37%)	0.587
8	12.16	13.598 (23.60%)	13.609 (23.62%)	13.933 (24.18%)	13.469 (23.38%)	13.652 (23.69%)	0.387
9	12.74	13.318 (23.12%)	13.074 (22.69%)	13.913 (24.15%)	13.240 (22.98%)	13.386 (23.23%)	0.717
10	13.52	14.016 (24.33%)	14.469 (25.16%)	15.027 (26.08%)	14.489 (25.15%)	14.507 (25.18%)	0.811

have a different degree of treatment on its own. This is best seen in Fig. 9 with the partially torrified and torrified pine. The partially torrefied material shows signs of proper heating around the outside of the material, while the middle is relatively untouched. Even the torrefied pine shows inhomogeneous character as there are still pockets of brown within the material.

Despite the variability, the HWI was able to give a single, meaningful characteristic to the bulk materials produced and was able to show a clear, significant, and sensitive difference in the level of heat treatment. Because of the significant sensitivity of the HWI, it is a powerful metric. One could easily envision this technique becoming a standard for not only the measurement of specific grinding energy for raw/treated biomass materials, but also for the determination of uniform bulk character between various treatments and industrial processes. This kind of metric is needed in industry for material uniformity testing/acceptance and is currently lacking. The HWI value itself should be proportionate to the energy needed to grind the material and the grinding order should be a good metric as to the general character of level of treatment between treatments of similar biomass materials. The HWI could be one of the tools used to ensure uniform product delivery between various biomass treatment processes and vendors. At this point, the direct relationships between measured parameters are not known well enough to form a standard, but further study could easily reveal them.

The level of effort involved in the HWI procedure is slightly more than the BWI procedure in that one has to determine the comminution order in addition to the grindability. However, for the widely varying properties of raw and treated biomass, this is critical. Fig. 6 shows that the comminution order of heat treated biomass materials is significantly higher than 1.5 and that the comminution order can shift with heat treatment. Therefore, one

Table 6
HWI test results, light pine.

Iteration	Grinding time (min)	Mass of undersize mill 1 (g)	Mass of undersize mill 2 (g)	Mass of undersize mill 3 (g)	Mass of undersize mill 4 (g)	Average (g)	95% Confidence (g)
0	11.00	13.186 (27.12%)	15.070 (31.00%)	15.103 (31.07%)	15.167 (31.20%)	14.632 (30.10%)	1.890
1	11.00	6.811 (14.01%)	6.839 (14.07%)	7.574 (15.58%)	7.461 (15.34%)	7.171 (14.75%)	0.789
2	20.72	7.576 (15.58%)	8.030 (16.52%)	8.039 (16.54%)	7.937 (16.33%)	7.596 (15.62%)	0.427
3	30.69	8.659 (17.81%)	8.721 (17.94%)	8.794 (18.09%)	8.925 (18.36%)	8.775 (18.05%)	0.224
4	39.80	8.978 (18.47%)	8.934 (18.38%)	8.912 (18.33%)	9.004 (18.52%)	8.957 (18.43%)	0.082
5	49.38	9.682 (19.92%)	8.968 (18.45%)	9.627 (19.80%)	9.532 (19.61%)	9.452 (19.45%)	0.644
6	58.27	10.440 (21.47%)	10.298 (21.18%)	10.545 (21.69%)	10.227 (21.04%)	10.378 (21.35%)	0.279
7	64.54	11.793 (24.26%)	11.088 (22.81%)	12.247 (25.19%)	11.400 (23.44%)	11.632 (23.93%)	0.983
8	66.45	11.825 (24.32%)	11.371 (23.39%)	11.812 (24.30%)	11.470 (23.59%)	11.620 (23.91%)	0.457
9	68.44	11.802 (24.28%)	12.000 (24.68%)	11.742 (24.15%)	11.784 (24.24%)	11.832 (24.34%)	0.225

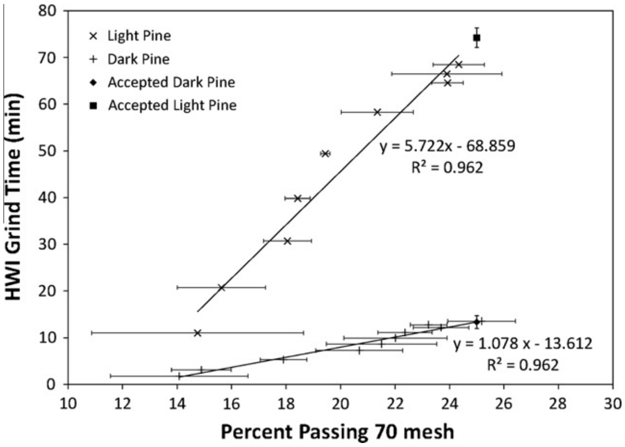

Fig. 7. HWI test plots to determine steady-state grinding time.

Table 7
Accepted steady-state HWI grinding time.

	Accepted grinding time (min)	95% Confidence interval (min)
Dark pine	13.33	1.37
Light pine	74.19	2.09

Table 8
Calculated HWI.

	HWI	95% Confidence interval
Dark pine	4265	438
Light pine	375,140	10,568

must supply the extra effort to determine these parameters for a given sample. Furthermore, it is likely that the comminution order will help segregate samples by level of treatment and could be a useful metric for material consistency.

In comparison to the RIM test, both the BWI and HWI are significantly more involved relative to the number of steps in a test. However, the RIM test requires sample of uniform starting geometry which are carefully prepared relative to the axis of the grain of wood and cannot use random geometries/orientations. Furthermore, the RIM test is a measure of mechanical integrity and not a measure of comminution energy. The two should be related, but they are not equivalent. It is not possible to predict comminution energy from the measured quantities in the RIM test. The RIM test was designed to detect fungal decay in wood, not for determining grinding energy [1–3]. That said, the RIM test does use the right energy level to selectively differentiate between levels of mechanical integrity. In fact, the originators of the RIM test used heat treatment as a surrogate for fungal decay (hemicellulose decomposition) and showed that their test could correlate mass loss caused by fungal decay and thermal decomposition to the measured RIM quantity [2]. It was for this reason that the high-energy ball mill was selected for this work and appears to be able to differentiate heat treatment levels which show up in the comminution order.

6. Future work

The current work was conducted with what materials were on hand and easily available. The purpose was to demonstrate the viability of the HWI in differentiating between various heat-treated materials. Clearly, the HWI has passed its proof of concept. Future work will focus on establishing the relationship between weight loss, chemical composition, and HWI parameters. A multiple kilogram fluid bed torrefaction system is nearing the final stages of shake down at NETL. This system will allow researchers the ability to generate carefully prepared samples in large enough quantities to measure the HWI at various heat treatment levels. The ability to generate uniform, carefully prepared samples at a large enough scale to be representative of industrial production should allow NETL to establish a production standard for industrial treatments. Further, plans for large-scale grindability testing are underway. The plans for large-scale testing involve a nineteen inch diameter, swing hammer mill that is custom modified to include shaft torque and speed measurements as well as a controllable variable speed drive. The mill has been sized such that it is the smallest scale possible that can represent much larger equipment in behavior and scaling metrics. Testing the same materials with the HWI and a large-scale mill will allow for positive correlation of the HWI for

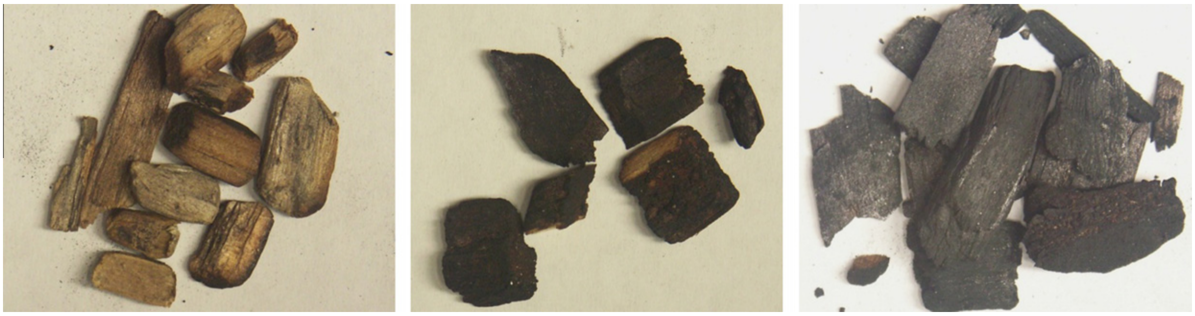

Fig. 8. Left: untorrefied pine; middle: partially torrefied pine; right: torrefied pine.

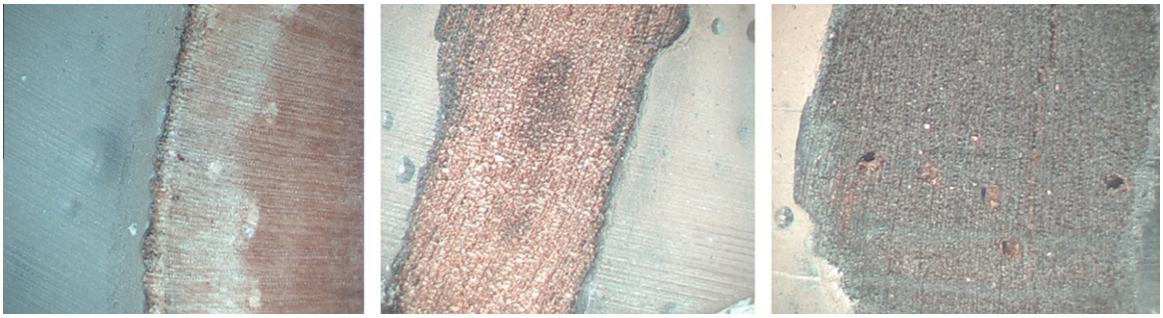

Fig. 9. Cross section of torrefied pine. left: untorrefied pine; middle: partially torrefied pine; right: torrefied pine.

specific grinding energy measurements within industry much like the BWI.

7. Conclusion

A modified BWI procedure was utilized with RIM to evaluate torrefied biomass materials. The new technique is known as the Hybrid Work Index (HWI) and is useful for assessing the grindability and general treatment character of both laboratory and industrially produced biomass materials. The hybridized procedure has been shown to be both highly correlated to energy consumption (proven now on the small scale) and sensitive to degree of torrefaction. The proposed HWI is certainly useful for assessing torrefaction in a laboratory environment, but it may also be correlated to grinding energy at industrial scale.

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